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ENVIRONMENTAL EFFECTS AND TREATMENT ALTERNATIVES FOR UREA RUNOFF--ETC(U)

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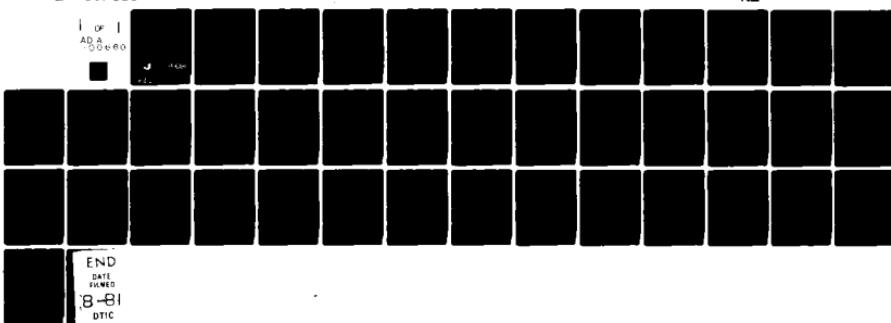
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**ENVIRONMENTAL EFFECTS AND  
TREATMENT ALTERNATIVES FOR  
UREA RUNOFF FROM AIRFIELD  
DE-ICING OPERATIONS**

ADA100660

**ROBERT G. BLUM  
ENVIRONMENTAL SCIENCES BRANCH**

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) <p>A literature review is presented which covers chemical transformation of urea, aquatic toxicity, nitrogenous oxygen demand and entrophication. Several feasible control technologies for urea runoff are examined, including source control, land application, trickling filter, breakpoint chlorination, and ammonia stripping.</p>																	

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## PREFACE

This report was prepared by the Environmental Sciences Branch of the Air Force Engineering and Services Center at Tyndall AFB, Florida 32403. The work was performed under Job Order Number (JON) 19007008 during the period from January 1979 to July 1980.

The project was originally to include field studies to gather hydrologic and water quality data for use in the development of a mathematical water quality model. However, due to very limited snowfall and urea use at the test site, the field studies (and hence, model development) could not be performed. The scope of the report was therefore limited to a literature review and examination of treatment alternatives for urea runoff from airfields.

This report has been reviewed by the Public Affairs Office (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication.

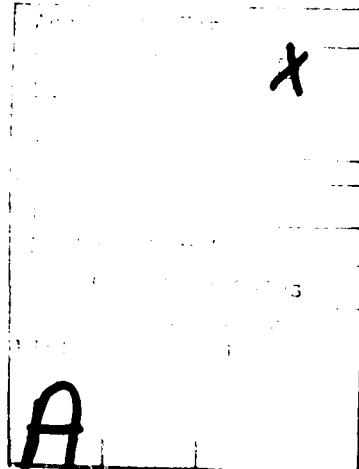
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## SECTION I

### INTRODUCTION

To sustain year-round flight operations at its northern bases, the U.S. Air Force uses large quantities of de-icing and anti-icing compounds. The chemical principally used for the prevention or removal of ice on airfield pavements is urea. The use of urea is not limited to the USAF but is commonly used at civilian and military air strips throughout the world. The compound is quite effective in preventing/removing the ice; however, when the snow and ice melt and become runoff, the urea can hydrolyze to ammonia which is highly toxic to most aquatic organisms. Several bases have reported fish kills caused by high ammonia concentrations in surface runoff which has been attributed to urea use. Other potential problems include: (1) Deoxygenation of a water course by nitrification of ammonia to nitrite, then nitrate; and (2) the production of nuisance algal blooms in aquatic systems which degrade water quality and accelerate the eutrophication process. Therefore, urea must be used only to the extent necessary to effect snow and ice removal with full knowledge of its potential adverse environmental effects. The objectives of this report are: (1) to impart this knowledge to users of this chemical, and those responsible for monitoring and protecting environmental quality; and (2) examine various pollution control alternatives.

A typical runway de-icing operation begins with the removal of as much snow as possible using mechanical methods (e.g., snow plows and airblast equipment). In order to prevent pavement damage, the snow and ice are shaved off to no less than 1/4 inch. The urea is then usually applied at the rate of one pound per 100 square feet (1/100 pound per square foot) over the center 50 feet of the runway. However, as much as 25 pounds per 100 square feet (1/4 pound per square foot) may be used depending on ice thickness

and temperature. Urea may be used for de-icing purposes at temperatures down to 15°F; however, its effectiveness is substantially reduced when temperatures are below the mid twenties (Reference 1).

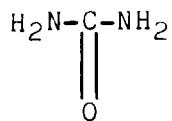
## SECTION II

### LITERATURE REVIEW

#### Chemistry of Urea

Urea is an important compound used in agricultural fertilizers and in the manufacture of drugs, synthetic resins, and plastics. It is also excreted in urine as an end-product from the metabolic breakdown of proteins in all living animals.

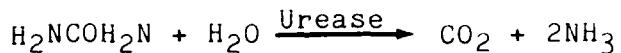
Urea (sometimes called carbamide) is a white crystal or powder with the following chemical structure:



It is manufactured by reacting ammonia with liquid carbon dioxide under elevated pressure and temperature.

#### Chemical Transformation of Urea

Urea readily hydrolyzes to carbon dioxide and ammonia in the presence of microorganisms containing the enzyme urease, according to the following reaction:



Evans, et al., (Reference 2) reported that in normal river water with 1 to 15 milligrams per liter (mg/l) urea, the above reaction rate was negligible below 8°C for up to 14 days; however, in river waters with high suspended solids, a maximum breakdown of 3 to 6 percent daily of the original urea levels occurred during the first

seven days. Complete degradation took place within 6 days for river samples at 20°C with high suspended solids.

A laboratory study by Atkinson (Reference 3) using river water at 5°C with 10 mg/l urea added showed that only 1 or 2 percent of the added urea hydrolyzed after 10 days.

Stiff and Gardiner (Reference 4) determined that the hydrolysis of urea (in samples containing the enzyme urease) was favored by increasing water temperature and pH. Under the unfavorable conditions of 0°C and pH 6.4, the authors also found that after three days the added urea was 81-percent hydrolyzed, and after six days it was 95-percent hydrolyzed. These experiments showed that urea hydrolysis was possible at winter temperatures at the pH values of river waters as long as urease or urease-active organisms are present. Additional laboratory experiments were performed at 5°C in a variety of river waters in the presence of bottom sediments. Although the authors could not explain the fluctuation in the urea concentration for one of the river samples, the remaining data indicated that the urea was almost completely hydrolyzed after a 14-day residence time.

Urea hydrolysis appears to proceed much more rapidly in soils. In an experiment designed to compare the nitrogen losses from urea and ammonium nitrate fertilizers in surface runoff waters, Moe, et al., (Reference 5) found that urea hydrolysis in soil was complete within one day.

Delaune and Patrick (Reference 6) determined that urea hydrolysis proceeded at an initial rate of about 8 to 12 ppm per hour and began to level off after about 24 hours in most of soils they studied. About 1/2 to 3/4 of the urea was converted to ammonia after 3 to 4 days of incubation. The maximum conversion of urea occurred at a soil pH of 8. They also found that the conversion

of surface-applied urea to ammonia in flooded soils took place in the soil and not in the flood water.

Sankhayan and Shukla (Reference 7) found that the hydrolysis of urea (in five soils of India) followed a first-order reaction. Most of the urea added to the soil samples was hydrolyzed within 24 hours.

Wagenet, et al., (Reference 8) reported that urea hydrolysis was independent of initial urea concentration and the oxygen concentration of the soil atmosphere.

Zantua, et al., (Reference 9) performed a study to determine the relationship between soil urease activity and other soil properties. They found that urease activity was highly correlated with organic carbon ( $r^*=0.72$ ), total nitrogen ( $r=0.71$ ) and cation-exchange capacity ( $r=0.67$ ), but was not significantly correlated with pH or alkalinity. Multiple regression analyses showed that organic matter content accounted for most of the variation in urease activity.

Based on the above review it is evident that the hydrolytic conversion of urea to ammonia will readily occur as long as urease-active microorganisms are present. Since flightline runoff generally flows over land or percolates through soil prior to reaching a drainage channel, any urea present will probably be transformed to ammonia in the process. If any urea remains in the runoff upon reaching a water course, it will ultimately be transformed to ammonia by urease-active organisms present in the sediment and/or suspended matter.

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\*  $r$  represents the correlation coefficient which has a range in value of -1 to +1.  $|r| = 1$  signifies perfect linear correlation;  $r=0$  signifies no correlation between the two variables.

## Toxicity

While urea itself exhibits minimal toxicity to aquatic life, its hydrolysis product - ammonia is highly toxic. Table 1 summarizes data on several fish and an insect used in aquatic bioassays. Generally, urea concentrations have to exceed several thousand milligrams per liter before significant biological effects are evident. As shown in Table 2, however, ammonia is toxic to fish at levels less than 1 mg/l. Ammonia toxicity has been attributed to the unprotonated form NH<sub>3</sub>, and not the ionized NH<sub>4</sub><sup>+</sup> specie. Therefore, higher pH and temperature, which favor the formation of the NH<sub>3</sub> ammonia specie, would be expected to increase toxicity.

TABLE 1. TOXICITY OF UREA TO AQUATIC ORGANISMS

<u>Organism</u>	<u>Urea (mg/l)</u>	<u>Exposure Time (hours)</u>	<u>Effect</u>	<u>Reference</u>
	<u>Concentration</u>			
Minnow	17.1	24	None	10
Creek Chub	30,000	24	Death	11
Rainbow Trout	1,500-5,000	*	Inhibitory	12
Fathead Minnow (Adult)	22,000-23,100	96	Death to 50%	13
Fathead Minnow (Fry)	20,000	96	Death to 50%	13
Giant Water Flea	11,000	96	Death to 50%	13

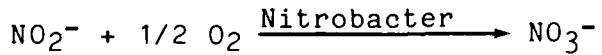
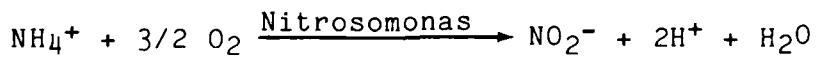
\* Not reported in reference

TABLE 2. TOXICITY OF AMMONIA TO AQUATIC ORGANISMS

<u>Organism</u>	Ammonia Concentration (mg/l as NH <sub>3</sub> -N)	Exposure <u>Time</u>	<u>Effect</u>	<u>Reference</u>
Rainbow Trout Fry	0.19	42 days	Blue Sac Disease	14
Rainbow Trout Fry	0.1	42 days	Growth Re- tardation	14
Chinook Salmon	0.002	6 weeks	Gill Hyper- plasia	15
Cutthroat Trout Fry	0.2-0.5	36 days	Death to 50%	16
Guppy Fry	1.26	72 hours	Death to 50%	17

Nitrogenous Oxygen Demand (NOD)

After urea hydrolyzes to ammonia, further biochemical reactions take place which utilize dissolved oxygen in the water. Certain bacteria can oxidize ammonia to nitrite (NO<sub>2</sub><sup>-</sup>), then nitrate (NO<sub>3</sub><sup>-</sup>) according to the following reactions:



These nitrifying organisms are classified as autotrophic and use CO<sub>2</sub> or HCO<sub>3</sub><sup>-</sup> as a carbon source. The stoichiometry of these equations indicates that theoretically, 4.57 grams of oxygen are

consumed per gram of ammonia-nitrogen ( $\text{NH}_4^+ \text{-N}$ ) oxidized to  $\text{NO}_3^-$ , assuming all the ammonia is oxidized to nitrate. In actual waters, it has been found that this ratio is somewhat lower because: (a) all the ammonia entering an aquatic system is not oxidized, and (b) oxygen is produced during  $\text{CO}_2$  fixation in the protoplasm synthesis of these microorganisms (Reference 18). Nevertheless, nitrification could have a significant effect upon the oxygen balance of a receiving water. For example, even assuming a low NOD ratio of 3 grams oxygen required per gram  $\text{NH}_4^+ \text{-N}$ , a stream with an  $\text{NH}_4^+ \text{-N}$  concentration of 2 mg/l would eventually lose 6 mg/l of dissolved oxygen (DO). This may cause the DO content of the stream to drop below the level necessary to sustain the life of aerobic organisms. The situation is especially critical during conditions of high temperature and low flow, when the DO content of most streams is initially low, and the hydrolysis of urea occurs at an increased rate.

#### Eutrophication

The entrance of urea and its associated nitrogenous degradation products into surface waters can result in excessive algal growth. (This is not surprising since urea is frequently used in plant fertilizers.) This phenomenon will occur if nitrogen is the only limiting nutrient in the aquatic system, which often is the case. (A survey performed by the Environmental Protection Agency (EPA) in 1972 showed that 30 percent of 623 lakes east of the Rocky Mountains were nitrogen limited.) Algal blooms can create a number of problems, including tastes and odors in drinking water and fish kills associated with algal toxins and/or oxygen depletion. Two groups of blue-green algae, Microcystis and Anabaena, produce toxins that can result in sickness or death to birds and mammals drinking the water (Reference 19).

The continued nourishment of a body of water (e.g., pond or lake) with excessive amounts of its limiting nutrient will result in an accelerated aging process. This is caused by the expired algal biomass and other organic matter which settles to the bottom and decays, gradually filling up the lake. The end result is a swamp, and eventually dry or boggy land.

### SECTION III

#### POLLUTION CONTROL TECHNIQUES

##### Discussion

Numerous schemes exist for the control of nitrogen compounds in wastewater. Table 3 summarizes the technically feasible methods, only a few of which are considered economically feasible for the control of urea runoff. Since the primary need is for a process which would remove/transform the ammonia component, those processes which are considered appropriate to treat urea runoff from airfields are:

- Land Application
- Conventional Secondary Treatment (Trickling Filter\*)
- Breakpoint Chlorination
- Ammonia Stripping

All the above options require the impoundment of the airfield runoff. The dams installed should be removable so that standing water will only be present during the winter season. (The type barriers presently used at some bases to control toxic substance spills would probably work well.) Depending upon the climate and topography which characterize the base, a series of these small impoundments may be necessary to contain the runoff and/or achieve the desired effluent quality in the discharge.

Although not considered a pollution control technique, the reduction or elimination of the use of urea for anti-icing/de-icing is

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\* Since most bases do not use the activated sludge process, this option is not considered.

TABLE 3. EFFECT OF VARIOUS TREATMENT PROCESSES  
ON NITROGEN COMPOUNDS (Source: Reference 20)

Treatment process	Effect on constituent			Removal of total nitrogen entering process, percent
	Organic N	NH <sub>3</sub> /NH <sub>4</sub>	NO <sub>2</sub>	
Conventional treatment processes				
Primary	10-20% removed	no effect	no effect	5-10
Secondary	15-25% removed <sup>b</sup> urea → NH <sub>3</sub> /NH <sub>4</sub>	< 10% removed	nil	10-20
Advanced wastewater treatment processes				
Filtration	30-95% removed	nil	nil	20-40
Carbon sorption	30-50% removed	nil	nil	10-20
Electrodialysis	100% of suspend organic N removed	40% removed	40% removed	35-45
Reverse osmosis	100% of suspend organic N removed	85% removed	85% removed	80-90
Chemical coagulation <sup>c</sup>	50-70% removed	nil	nil	20-30
Land application				
Irrigation	NH <sub>3</sub> /NH <sub>4</sub>	NO <sub>2</sub> plant N	plant N	40-90
Infiltration/percolation	NH <sub>3</sub> /NH <sub>4</sub>	NO <sub>2</sub>	N <sub>2</sub>	0-50
Major nitrogen removal processes				
Nitrification	limited effect	NO <sub>2</sub>	no effect	5-10
Denitrification	no effect	no effect	80-88% removed	70-95
Breakpoint chlorination	uncertain	90-100% removed	no effect	80-95
Selective ion exchange for ammonium	some removal, uncertain	95-97% removed	no effect	80-95
Ammonia stripping	no effect	60-95%	no effect	50-90
Other nitrogen removal processes <sup>a</sup>				
Selective ion exchange for nitrate	nil	partial transformation to NH <sub>3</sub> /NH <sub>4</sub>	partial removal by stripping	75-90% partial removal by nitrification
Oxidation bonds				denitrification cells
Algae stripping	partial transformation to NH <sub>3</sub> /NH <sub>4</sub>	cells	cells	50-80
Bacterial assimilation	no effect	40-70% removed	limited effect	30-70

a Will depend on the fraction of influent nitrogen for which the process is effective, which may depend on other processes in the treatment plant.  
 b Soluble organic nitrogen, in the form of urea and amino acids, is substantially reduced by secondary treatment.  
 c May be used to remove particulate organic carbon in plants where ammonia or nitrate are removed by other processes.

certainly an alternative solution. Therefore, several options under this category are examined in the next subsection, Source Control.

#### Source Control

The most obvious way to reduce the adverse environmental effects of urea is to control its use. Air Force Manual (AFM) 91-14\* prescribes a maximum application of 0.01 lb/ft<sup>2</sup>. Atkinson (Reference 3) reported a urea usage of approximately 1 kilogram per 40 square meters (0.0051 lb/ft<sup>2</sup>) at Linton Airfield (RAF) was sufficient if applied ahead of falling temperature. If the ice is inadvertently or unknowingly allowed to form, up to 4 times this quantity may be necessary to obtain wet runways. Stiff and Gardiner (Reference 4) stated that the use of urea by the RAF is restricted to prevention of ice formation (anti-icing) rather than removal of ice already present (de-icing). The urea is spread over runways and servicing areas prior to an expected frost. AFM 91-14 does, in fact, recommend that anti-icing procedures be used whenever possible to prevent the formation of ice. Bases should also ensure that only the minimum quantity of urea is applied to melt the snow and ice.

Ice sensor systems are available which can predict frost and ice conditions before they actually occur on bridges, highways and airport runways. The manufacturer's literature (Reference 21) indicates that the systems have been successfully used at several airfields. Such a system might be useful at certain USAF bases to alert snow and ice control crews to initiate anti-icing measures, and therefore effect a reduction in the amount of urea used.

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\* This manual will be superseded in the near future by AFR 91-5 which is presently being coordinated with the Major Air Commands.

Another method for reducing the impact of urea would be the substitution of a less environmentally degrading chemical, or an entirely different method to de-ice airfields. Other chemicals known for their de-icing ability are isopropyl alcohol, formamide, and ethylene glycol. Isopropyl alcohol has limited use because it is deleterious to acrylic plastics normally used in aircraft canopies and windows; formamide is more toxic to aquatic life than the other de-icing compounds and has not yet been approved by the Air Force Materials Laboratory; and ethylene glycol is much more expensive to use than urea and can cause significant deoxygenation in receiving waters. Other methods which might eliminate the use of urea involve the utilization of airfield pavement heating systems. Pravda, et. al., (Reference 22) investigated the economics of electrical, oil-fired steam, and solar-heated pavement systems. The authors concluded that the capital and annual operating costs for an electrically-heated runway are the highest; the capital cost for a steam-heated runway is lower than either the electrical or solar systems; and the annual operating cost of the solar system is the lowest for the range of pavement areas represented by runways and ramps. Minsk (Reference 23) developed an electrically-conductive asphaltic concrete which could pass an electric current, thereby generating sufficient heat to prevent the accumulation of snow and ice on the surface. Lane and Marshall (Reference 24) investigated the use of lasers to de-ice remote surfaces. They found that a single pulse delivered to the interface between the ice and its substrate (substrates tested were asphalt, concrete, brass, aluminum, steel and stone) at a power density of  $10^8$  to  $10^9$  watts per square centimeter, produced fractures of 0.1 to 2 centimeters diameter for all substrates. According to the authors, if the initial fracture could be propagated by suitable scanning of the optical beam over the interface, the ice could be disrupted, and then easily removed from the surface.

Specific cost data for the above airfield heating systems could not be obtained, but it is judged that they would be far more costly (at existing airfields) than the use of de-icing/anti-icing chemicals. However, they could be cost-effective if installed during the construction of a new runway: or if the energy were provided by wind turbines, solar systems, waste steam/POL (petroleum, oil, and lubricants), or perhaps a combination of these. A cost analysis (based on a 10-percent discount rate, a 20-year economic period, and assuming that the cost of urea can be approximated as a uniform series of annual payments) shows that for such a system to be cost-effective, its capital cost must be less than 8.5\* times the base's annual expenditure on urea. For example, if a base is using 500,000 pounds of urea per year (at \$10.40 per 100 pounds) then this base should consider replacing urea use with a solar/waste steam/wind turbine/waste POL pavement heating system only if the capital outlay for this system is less than \$442,000.

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\* This represents a "ballpark" figure since miscellaneous operation, maintenance, and replacement (OMR) costs associated with these alternatives is not taken into consideration, as well as the "cost" of environmental quality degradation (or cost of pollution control techniques) associated with urea use. The figure also varies with the discount rate (and the economic analysis period selected). For example, at a 15-percent discount rate the value is 6.3; at 5 percent it is 12.5. Since urea use is an annualized expenditure it becomes more economically favorable at higher discount (interest) rates when compared to an alternative with high capital/low annual costs. If the capital cost for the pavement heating system considered is about equal to or less than 8.5 times the annual cost of urea, then a more detailed cost analysis should be performed which includes OMR costs, pollution control costs, and uses the current discount rate in comparing the two alternatives.

### Land Application (Irrigation)

As previously stated, nitrogen is an important nutrient for the survival and growth of all plants. Once the urea decomposes to inorganic form (i.e.,  $\text{NH}_4^+$  or  $\text{NO}_3^-$ ) it becomes available for uptake by plants.

Metcalf and Fddy, Inc. (Reference 25) reported that between 60 and 90 percent of total nitrogen in wastewater applied as land irrigation is removed in the process. (This assumes that the crops which absorb the nitrogen are physically removed by harvesting.) Table 4 shows the nitrogen removals of various forage crops (extracted from Reference 25). In addition to its utilization by plants, some of the nitrate is reduced to nitrogen gas and nitrous oxide by certain bacteria. This process is called denitrification and occurs in water-logged soils or natural waters that have become deficient in oxygen. Also, some of the nitrogen present as dissolved ammonia gas ( $\text{NH}_3$ ) will volatilize to the atmosphere.

TABLE 4. NITROGEN UPTAKE BY VARIOUS FORAGE CROPS (Source: Ref 25)

Type of Vegetation	Description	Dry Matter yield, Kg/ha	Nitro- gen, Kg/ha
Alfalfa	Perennial legume	15,770	504
Brome grass	Cool-season perennial	9,856	186
Coastal Bermuda Grass	Warm-season perennial	19,712	560
Reed Canary Grass	Cool-season perennial	13,000	350
Ryegrass	Cool-season annual or perennial	8,030	235
Sweet Clover	Biennial legume	7,375	177
Tall Fescue	Cool-season perennial	6,854	133

One potential problem in treating this nitrogenous runoff water by land application is that some nitrates ( $\text{NO}_3^-$ ) may leach into the groundwater. If this groundwater is used for water supply, precautions would have to be taken to ensure that nitrate levels remain below 45 mg/l\* as  $\text{NO}_3^-$  (equivalent to 10 mg/l as  $\text{NO}_3^- - \text{N}$ ). The rationale for this standard is the implication of nitrates in drinking water in the disease methemoglobinemia in infants under 3 months of age (Reference 26).

Runoff water from runways and taxiways might also contain phenols (from the degradation of aircraft fuel residues), trace metals, and various oils. Therefore, this water should not be used to irrigate food crops for humans or livestock. Suitable irrigation areas would be the base golf course or forest land, for example.

Periods of snow cover and subfreezing conditions may limit irrigation to forest land and perennial grasses. According to Metcalf and Eddy, Inc. (Reference 25), this depends on water quality criteria for the infiltrating water since the treatment efficiency of soil systems decreases under these conditions. Wastewater irrigation systems can usually operate successfully below  $0^\circ\text{C}$ , as evidenced by a forest irrigation system at Dover, Vermont, which operates at temperatures down to  $-12.2^\circ\text{C}$ .

It should be emphasized that the majority of the applied nitrogen will only be removed if the crops assimilate it and are subsequently removed by harvesting. Otherwise, the plants will simply die, returning the stored organic nitrogen to the soil and starting the cycle anew. The most important function served by irrigating with urea runoff is that the ammonia is removed by plant uptake and bacterial oxidation. Since ammonia ( $\text{NH}_3$ ) is the

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\* This represents the maximum containment level (MCL) which has been established by the EPA under the Safe Drinking Water Act.

most toxic specie to aquatic organisms this treatment process will protect life in the watercourse. On the other hand, it has the negative impact of potentially raising nitrate levels in the groundwater.

This option would probably require pumping the runoff water from the holding ponds to the area(s) to be irrigated and an irrigation system. However, if the land area(s) selected are at a lower elevation than the holding ponds, a gravity flow system may be possible.

#### Trickling Filter

According to Table 3, less than 10 percent of the  $\text{NH}_3/\text{NH}_4$  content is removed by conventional secondary treatment. However, several steps can be taken to improve the nitrifying capacity of a trickling filter. The two most economical are: (1) use of a different filter media and (2) increased recirculation. Of course, the first step should always be a review of present plant operation to improve performance through better maintenance, proper operating techniques, or equipment repair.

The growth and maintenance of nitrifying organisms in a trickling filter are dependent on a number of factors including organic loading, pH, dissolved oxygen, temperature, and the presence of toxicants. An increase in organic loading will decrease nitrification efficiency since the heterotrophic bacterial population will grow and displace the nitrifiers. For rock media, attainment of 75-percent nitrification or better requires the organic loading to be limited to 10 to 12 pounds  $\text{BOD}_5/1000$  cubic feet/day (0.16 to 0.19 kilograms/cubic meter/day) (Reference 20). At higher organic loading rates the degree of nitrification is reduced, and above 30 to 40 pounds  $\text{BOD}_5/1000$  cubic feet/day (0.48 to 0.64 kilogram/cubic meter/day), very little nitrification occurs (Reference 20). The

literature sources investigated in this study reported that the optimum pH value for nitrification is between 6 and 9 (References 27 - 32). The dissolved oxygen effect has been modeled by the Monod relationship (considering oxygen to be a growth limiting substrate) as follows:

$$u_N = \hat{u}_N \frac{DO}{K_{O_2} + DO}$$

where:

DO = dissolved oxygen concentration (mg/l)

$K_{O_2}$  = half-saturation constant for oxygen (mg/l)

$u_N$  = Nitrosomonas growth rate (day<sup>-1</sup>)

$\hat{u}_N$  = Peak Nitrosomonas growth rate (day<sup>-1</sup>)

Two values of  $K_{O_2}$  were reported to be 1.3 mg/l and 2.0 mg/l by two different investigators (Reference 20). The optimum temperature range for nitrification has been reported by several sources (References 32-35) as 25° to 35°C, and Bansal (Reference 35) reported that heterotrophs have optimum growth at 18° to 25°C. Also, certain heavy metals and organic compounds are toxic to nitrifiers.

By replacing rock media with plastic media, the capacity of a trickling filter can be greatly increased. The plastic media have a large specific surface area (approximately twice that of rock media) which allows greater slime surface per unit volume. In addition, the light weight of the media permits construction of filters up to 25 feet deep, as compared with 5 to 6 feet for rock filters.

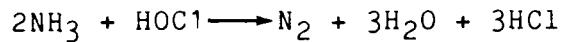
Increasing recirculation might also be effective in improving the nitrification capacity of the filter. Especially in those cases

where the trickling filter is lightly loaded (organically), increasing recirculation might allow the same filter to act as a second-stage nitrification filter.

The main drawbacks to this alternative are: (a) some Air Force trickling filters may be overloaded organically, which would inhibit the establishment of a nitrifier population on the filter media; (b) the temperature of the combined urea runoff and base wastewater would probably be quite low as a result of low ambient temperatures during the winter season (therefore, the nitrification rate would be extremely low); and (c) the hydraulic capacity of the trickling filter may not be sufficient to handle the periodic discharge of urea runoff to the treatment plant. Therefore, the usefulness of the trickling filter option for urea runoff control would have to be determined on a case-by-case basis.

#### Breakpoint Chlorination

Chlorine reacts with ammonia in a step-wise fashion to ultimately produce nitrogen gas, water, and hydrochloric acid, according to the following reaction:



Stoichiometrically, the mass ratio of chlorine (as  $\text{Cl}_2$ ) to ammonia (as N) is 7.6:1; however, in practice the actual mass ratio required to oxidize all the ammonia (i.e., achieve breakpoint chlorination) ranges from 8:1 to 10:1. That is, if the urea runoff in the holding pond has an  $\text{NH}_3\text{-N}$  concentration of 10 mg/l, then about 100 mg/l of  $\text{Cl}_2$  would be needed to completely remove it.

In laboratory studies at Blue Plains (Reference 20), the optimum pH for breakpoint chlorination was determined to be 6 to 7. If

breakpoint chlorination occurs outside this range, it was observed that the chlorine requirement is higher and the reaction rate is slower. There is no evidence that normal temperature variations of wastewater effluents have any effect upon breakpoint chlorination.

The breakpoint chlorination process increases the acidity of the treated water, which either must be sufficiently buffered or supplemented with a source of alkalinity. Stoichiometrically, 14.3 mg/l of alkalinity (as  $\text{CaCO}_3$ ) is consumed for each 1.0 mg/l of ammonia nitrogen which is oxidized; but in actual practice about 15 mg/l of alkalinity is consumed. The compounds most commonly used to supplement the natural alkalinity for pH control are sodium hydroxide ( $\text{NaOH}$ ) and lime ( $\text{CaO}$ ). If all the acidity generated in the breakpoint reaction is to be neutralized, then 1.50 parts of  $\text{NaOH}$  are needed for each part of  $\text{Cl}_2$ , or 1.05 parts of  $\text{CaO}$  for each part  $\text{Cl}_2$ . Since the buffering capacity of most runoff waters is negligible, this neutralization process may be necessary subsequent to the breakpoint chlorination of urea airfield runoff.

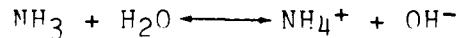
The breakpoint chlorination process will also increase the total dissolved solids (TDS) in the treated water. Therefore, this process should not be used if stream standards for TDS would be exceeded.

Previous studies have shown that breakpoint chlorination results in slight to partial removal of organic nitrogen (References 36 and 37). Therefore, if this option is selected, it must be ensured that the majority of urea in the holding pond has hydrolyzed to ammonia. The retention time required to accomplish this may or may not be possible, depending upon a variety of factors such as runoff rate, holding capacity, temperature, sediment bacteria, and pH.

Another drawback to this scheme is that precise chlorine dosage and pH control are required in order to obviate the need for a dechlorination step. Since chlorine is even more toxic to aquatic life than ammonia, the possibility exists that this process could degrade rather than purify the water, and is therefore not recommended for the treatment of urea runoff.

#### Ammonia Stripping

Ammonia and ammonium ions are in equilibrium in water as shown in the following equation:



As the pH increases, the reaction is driven to the left, increasing the NH<sub>3</sub> fraction. At a pH value of 11, essentially all of the ammonium is converted to NH<sub>3</sub> gas. This gas can then be removed by stripping with a clean gas (i.e., one that does not contain ammonia). Air is normally used as the clean gas because of its availability and the large quantities usually required in the stripping process.

A major problem with ammonia stripping is the effect of low temperatures on the process. As the water temperature decreases, the solubility of ammonia in water increases, making it more difficult to remove by means of stripping. Since this process would be used on cold runoff water, this temperature effect could present a major drawback. Another problem with ammonia stripping towers is the control of scaling in the tower packing material resulting from calcium carbonate deposition. Also, the highly alkaline water must be neutralized prior to release.

Perhaps a more economical and less troublesome method for ammonia stripping would be to use stripping ponds. Stripping ponds have

been successfully used in Israel (Reference 38), and the South Tahoe advanced wastewater treatment facility has modified its processes to incorporate these ponds. Pilot tests at South Tahoe have shown that the release of ammonia from the high pH ponds is accelerated by surface agitation. The South Tahoe ponds have detention times of 7 to 18 hours and are agitated and recycled by pumping the water through vertical spray nozzles. They expect to achieve 37 percent ammonia removal from the ponds alone, even in cold weather conditions. The ponds at this facility are followed by a forced-draft tower and breakpoint chlorination, yielding essentially complete nitrogen removal.

There are two potential environmental impacts from the use of ammonia stripping ponds:<sup>\*</sup> air pollution and ammonia washout from the atmosphere. A typical ammonia concentration in a stripping tower discharge is about 6 milligrams per cubic meter ( $\text{mg}/\text{m}^3$ ).

The odor threshold for  $\text{NH}_3$  is  $35 \text{ mg}/\text{m}^3$ ; eye, nose, and throat irritation is reported to occur above  $280$  to  $490 \text{ mg}/\text{m}^3$ . Concentrations of  $700 \text{ mg}/\text{m}^3$  can have adverse effects on plants; and human or animal toxicities begin to occur at  $1700$  to  $4500 \text{ mg}/\text{m}^3$ . Ammonia in the atmosphere is relatively stable and will not react to form nitrogen oxides. However, it can react with sulfur dioxide (e.g., from a fossil-fuel power plant) and water to form an ammonium sulfate aerosol. Regulatory agencies in the U.S. have not established ammonia emission standards since there are no known public health implications at concentrations normally encountered. However, a few countries have established ambient air standards for ammonia. For example, the USSR and Czechoslovakia have

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\* If ammonia stripping towers are used, then noise would be another environmental consideration.

established a basic standard of 0.2 mg/m<sup>3</sup> and 0.1 mg/m<sup>3</sup>, respectively, during a 24-hour period (Reference 20). The American Conference of Governmental Industrial Hygienists has adopted (1979) an occupational threshold limit of 18 mg/m<sup>3</sup> (Reference 39).

Atmospheric ammonia is returned to the earth through gaseous deposition (60 percent), aerosol deposition (22 percent), and precipitation (18 percent) (Reference 20). Since the amount of ammonia in rainfall is directly related to the concentration of ammonia in the atmosphere, the gaseous ammonia in the vicinity of the stripping pond could be deposited on the earth. The portion of the rainfall landing on soils would have the same fate as in land application. However, that portion falling on paved areas or bodies of water would appear in the runoff and could thus impact on water quality. Unless the stripping pond is located close to a lake or reservoir, it is very unlikely that any significant impact would result. However, the above environmental considerations should be carefully evaluated prior to application of the stripping process.

## SECTION IV

### CONCLUSIONS AND RECOMMENDATIONS

1. The toxicity of ammonia to aquatic life is the most critical environmental effect of the use of urea for airfield snow and ice control. Ammonia in water can exist as two species -  $\text{NH}_4^+$  (ammonium ion) and  $\text{NH}_3$  (dissolved ammonia gas), the proportional distribution of which is a function of pH and temperature.  $\text{NH}_3$  is the highly toxic specie, and its fraction increases with increasing pH and temperature. A water quality criterion of 0.02 mg/l  $\text{NH}_3$  has been established for the protection of aquatic life.
2. Other environmental effects of the use of urea are: (1) the exertion of oxygen demand in aquatic systems due to the aerobic nitrifying bacteria which oxidize ammonia to nitrate and (2) the production of nuisance algal blooms which degrade water quality and accelerate the entrophication process in a body of water.
3. The most effective and economical way to reduce the adverse environmental effects of urea is to control its use. Policies and procedures prescribed in AFM 91-14 (soon to be superseded by AFR 91-15) should be strictly adhered to. In particular, anti-icing (ice prevention) as opposed to de-icing (ice removal) procedures should be employed whenever possible since it requires far less urea.
4. An ice sensor system which predicts frost and ice conditions should be employed at those bases which routinely engage in snow and ice removal operations during the winter. This system will enable the base to maximize its use of anti-icing (as opposed to de-icing) procedures.

5. Urea-using air bases which are drained by streams with high winter flows will probably not require any treatment of the urea runoff water. However, in those locations where adequate dilution is not afforded, treatment of this runoff may be required.

6. Ammonia concentrations in receiving waters on, or adjacent to, the urea-using base should be periodically monitored during the snow and ice season. If the  $\text{NH}_3$  concentration exceeds the criterion of 0.02 mg/l, then treatment measures should be considered.

7. If treatment measures are required, then the most cost-effective method would probably be land application of the runoff water. Other techniques which could be utilized are routing the runoff through a secondary (or better) wastewater treatment plant, breakpoint chlorination, or ammonia stripping, the latter two being the most costly.

a. Land application would probably require pumping from the ponds to the area(s) of application and some type of irrigation/distribution system. This method would result in essentially all ammonia-nitrogen being converted to some other form (such as nitrate, nitrogen gas, or organic nitrogen in plant cells) or volatilizing to the atmosphere. One potential problem with land application is that if the water contains more nitrogen than the soil organisms and plants can utilize, then the remainder will leach into the groundwater. If this groundwater is subsequently used for water supply, then it must be ensured that nitrate levels are below 45 mg/l as  $\text{NO}_3^-$  (or the standard set by the host country).

b. Routing the runoff through the wastewater treatment plant (trickling filter is assumed) might be feasible in certain cases. For best results the trickling filter should be organically and

hydraulically underloaded, rock media should be replaced with plastic media, and recirculation to the filter should be increased. However, even if all these conditions prevail it is unlikely that more than 30 percent of the ammonia will be nitrified to nitrate, due to cold temperatures which would prevail during the snow and ice season. This option would probably also involve the pumping of water from the ponds to the treatment plant.

c. Breakpoint chlorination could be used to remove all the ammonia-nitrogen present in the urea runoff. This would require the addition of about 9 parts Cl<sub>2</sub> per part NH<sub>3</sub>-N by weight. The breakpoint chlorination process would increase the acidity of the water, and might require chemical addition for neutralization prior to discharge. Total dissolved solids (TDS) would also increase (from chlorine and alkalinity addition); therefore TDS standards in the host country should be checked to ensure compliance if this process is used. The process would require a chlorine feed system and a mixer immersed in the pond. The most significant drawbacks for this option are that strict control and monitoring of chlorine dosage would be required. Since chlorine is even more toxic to aquatic organisms than ammonia, any overdose of chlorine would quickly make the "cure worse than the disease" for this scheme. Therefore, this process is not recommended for use in treating urea runoff from airfields.

d. The ammonia stripping option would be most economical in ponds rather than conventional stripping towers. Even so, this process would probably be the the most costly alternative because of the need for a surface agitation system, lime or caustic to raise the pH to over 11, and acid (e.g., H<sub>2</sub>SO<sub>4</sub>) to neutralize the water prior to discharge. Ammonia removal efficiency for this

process is substantially reduced at low temperatures. The application of this process also presents the potential for environmental impact on air and water quality in the vicinity of the stripping ponds. Due to these problems and its high cost, ammonia stripping is not recommended for use in controlling pollution from urea runoff.

e. All the above treatment schemes would involve the construction of a series of impoundments on the airfield drainage channels. The dams used to create these impoundments should be removable types in order to prevent the accumulation of standing water during the warmer months.

8. The literature shows that urea readily hydrolyzes to ammonia in the presence of urease-active organisms which primarily inhabit soils, aquatic sediments, or suspended solids. However, in the absence of these organisms, the rate of hydrolysis is negligible. In view of this finding, the holding time for the urea runoff in the impoundments should be adjusted such that the majority of the urea is hydrolyzed to ammonia prior to treatment. This is particularly important for the breakpoint chlorination and ammonia stripping options for which the effects of the treatment process on organic nitrogen (e.g., urea) are uncertain and nil, respectively.

9. Research and development efforts should be initiated to find cost-effective methods for ice prevention/removal on airfields which would be less environmentally degrading than urea. Other de-icing compounds are either much more expensive than urea, or cause undesirable environmental effects. The use of pavement heating systems is a possible avenue of research although capital costs for such systems would probably be quite high. However, if alternative energy schemes are utilized these systems may be more economical than urea use. (For example, power sources for the

systems could be a series of large batteries charged by wind turbines and/or photovoltaic cells. An auxiliary or back-up power source might consist of a generator powered by waste POL.) Further research into the use of lasers for fracturing surface ice should also be conducted.

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